

What is claimed is:

1. A process for producing chlorine by oxidizing hydrogen chloride with oxygen, wherein said process uses one catalyst selected from the following catalysts (1) to (9):

(1) a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a basic compound, treating by using a reducing compound, and oxidizing;

(2) a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing agent to form ruthenium having an oxidation number of 1 to less than 4 valence, and oxidizing;

(3) a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, reducing the supported one by using a reducing hydrogenated compound, and oxidizing;

(4) a supported ruthenium oxide catalyst obtained by using titanium oxide containing rutile titanium oxide as a carrier;

(5) a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a

reducing compound or reducing agent in a liquid phase, and oxidizing, wherein titanium oxide contains an OH group in an amount of  $0.1 \times 10^{-4}$  to  $30 \times 10^{-4}$  (mol/g-carrier) per unit weight of the carrier;

(6) a catalyst system containing the following components (A), and not less than 10% by weight of component (B):

(A) an active component of catalyst;

(B) a compound wherein thermal conductivity of a solid phase measured by at least one point within a range from 200 to 500°C is not less than 4 W/m.°C;

(7) a supported ruthenium oxide catalyst having a macro pore with a pore radius of 0.03 to 8 micrometer;

(8) an outer surface-supported catalyst obtained by supporting ruthenium oxide on a carrier at the outer surface; and

(9) a supported ruthenium catalyst obtained by using chromium oxide as a carrier.

2. The process according to claim 1 (1), wherein the reducing compound is a compound selected from the group consisting of hydrazine, methanol, ethanol, formaldehyde, hydroxylamine, formic acid and compounds having a oxidation-reduction potential of -0.8 to 0.5 v.

3. The process according to claim 1, wherein the catalyst (2) is a supported ruthenium oxide catalyst

obtained by the steps which comprise supporting at least one ruthenium compound selected from the group consisting of ruthenium halide, chlororuthenate salt, oxyruthenate salt, rutheniumoxy chloride, ruthenium-ammine complex, chloride of ruthenium-ammine complex, ruthenium acetylacetonato complex, ruthenium organic acid salt and ruthenium-nitrosyl complex on a carrier, treating the supported one by using a reducing agent to form ruthenium having an oxidation number of 1 to less than 4 valence, and oxidizing.

4. The process according to claim 1, wherein the catalyst (2) is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting at least one ruthenium compound selected from the group consisting of ruthenium halide, chlororuthenate salt, oxyruthenate salt, rutheniumoxy chloride, ruthenium-ammine complex, chloride of ruthenium-ammine complex, ruthenium acetylacetonato complex, ruthenium organic acid salt and ruthenium-nitrosyl complex on a carrier, treating the supported one by using a basic compound, treating by using a reducing agent, and oxidizing.

5. The process according to claim 1 (2), wherein the reducing agent is a reducing compound.

6. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst

obtained by supporting ruthenium halide on a carrier, treating the supported one by using hydrazine, methanol, ethanol or formaldehyde, and oxidizing.

7. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by supporting a ruthenium compound on a carrier, treating the supported one by using an alkali solution of hydrazine, methanol, ethanol or formaldehyde, and oxidizing.

8. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by supporting a ruthenium compound on a carrier, treating the supported one by using an alkali, treating by using a reducing compound, and oxidizing.

9. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst prepared by supporting a ruthenium compound on a carrier, treating the supported one by using an alkali solution of a reducing compound, and oxidizing.

10. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by supporting ruthenium halide on a carrier, treating the supported one by using an alkali, treating by using hydrazine, methanol, ethanol or formaldehyde, and oxidizing.

11. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by supporting ruthenium halide on a carrier, treating the supported one by using an alkali solution of hydrazine, methanol, ethanol or formaldehyde, and oxidizing.

12. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by supporting ruthenium halide on a carrier, treating the supported one by adding an alkali, treating by using hydrazine, and oxidizing.

13. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by supporting ruthenium halide on a carrier, treating the supported one by using an alkali solution of hydrazine, and oxidizing.

14. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by supporting ruthenium halide on a carrier, treating the supported one by adding an alkali, treating with hydrazine, adding an alkali metal chloride, and oxidizing.

15. The process according to claim 1, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by supporting ruthenium halide on a carrier,

treating the supported one by using an alkali solution of hydrazine, adding an alkali metal chloride, and oxidizing.

16. The process according to claim 1, wherein the catalyst (3) is a supported ruthenium oxide catalyst obtained by supporting a ruthenium compound on a carrier, reducing the supported one by using a reducing hydrogenated compound, and oxidizing.

17. The process according to claim 1, wherein the catalyst (3) is a supported ruthenium oxide catalyst obtained by supporting a ruthenium compound on a carrier, reducing the supported one by using a reducing hydrogenated compound, adding an alkali metal chloride, and oxidizing.

18. The process according to claim 1, wherein the catalyst (3) is a supported ruthenium oxide catalyst obtained by supporting ruthenium halide on a carrier, reducing the supported one by using an alkali metal boron hydride compound, and oxidizing.

19. The process according to claim 1, wherein the catalyst (3) is a supported ruthenium oxide catalyst obtained by supporting ruthenium hydride on a carrier, reducing the supported one by using an alkali metal boron hydride compound, adding an alkali metal chloride, and oxidizing.

20. The process according to claim 1, wherein the catalyst (3) is a supported ruthenium oxide catalyst

obtained by supporting ruthenium chloride on a carrier, reducing the supported one by using sodium boron hydride, and oxidizing .

21. The process according to claim 1, wherein the catalyst (3) is a supported ruthenium oxide catalyst obtained by supporting ruthenium chloride on a carrier, reducing the supported one by using sodium boron halide, adding an alkali metal chloride, and oxidizing.

22. The process according to claim 1, wherein the catalyst (1), (2) or (3) is a supported ruthenium oxide catalyst obtained by using titanium oxide containing not less than 10% by weight of rutile titanium oxide as a carrier.

23. The process according to claim 1, wherein the catalyst (1), (2) or (3) is a supported ruthenium oxide catalyst obtained by using titanium oxide containing not less than 30% by weight of rutile titanium oxide as a carrier.

24. The process according to claim 1, wherein the catalyst (4) is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $0.1 \times 10^{-4}$  to  $30 \times 10^{-4}$  (mol/g-

carrier) per unit weight of a carrier is used as the carrier.

25. The process according to claim 1, wherein the catalyst (4) is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $0.2 \times 10^{-4}$  to  $20 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

26. The process according to claim 1, wherein the catalyst (4) is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $3 \times 10^{-4}$  to  $15 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

27. The process according to claim 1, wherein the catalyst (4) or (5) is a supported ruthenium oxide catalyst obtained by using titanium oxide containing not less than 10% by weight of rutile titanium oxide as a carrier.

28. The process according to claim 1, wherein the catalyst (4) or (5) is a supported ruthenium oxide catalyst obtained by using titanium oxide containing not less than 30% by weight of rutile titanium oxide as a carrier.



29. The process according to claim 1, wherein the catalyst (5) is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $0.2 \times 10^{-4}$  to  $20 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

30. The process according to claim 1, wherein the catalyst (5) is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $3 \times 10^{-4}$  to  $15 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

31. The process according to claim 1, wherein the catalyst (4) or (5) is a supported ruthenium oxide catalyst obtained by supporting a ruthenium compound on a carrier, reducing the supported one by using a reducing hydrogenated compound, and oxidizing.

32. The process according to claim 1, wherein the catalyst (4) or (5) is a supported ruthenium oxide catalyst obtained by supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound,

and oxidizing.

33. The process according to claim 1, wherein the catalyst (4) or (5) is a supported ruthenium oxide catalyst obtained by supporting a ruthenium compound on a carrier, treating the supported one by using an alkali solution of a reducing compound, and oxidizing.

34. The process according to claim 1, wherein the catalyst system (6) is a catalyst system at least containing a component (A), a component (B) and a catalyst carrier component.

35. The process according to claim 1, wherein the catalyst system (6) is a catalyst made of a molding containing a component (A) and a component (B) obtained by integrally molding.

36. The process according to claim 1, wherein the catalyst system (6) is a catalyst made of a molding containing a component (A), a component (B) and a catalyst carrier component obtained by integrally molding.

37. The process according to claim 35, wherein the catalyst is made of a molding containing the component (A) supported on the component (B).

38. The process according to claim 36, wherein the catalyst is made of a molding containing both the component (A) supported on the catalyst carrier component and the component (B).

39. The process according to claim 36, wherein the catalyst is made of the molding containing the component (A) supported on a mixture of the catalyst carrier component with the component (B)

40. The process according to claim 1, wherein the catalyst system (6) is a catalyst system containing both of a molding containing the component (A) and the component (B) obtained by integrally molding and a molding containing the component (B) obtained by integrally molding.

41. The process according to claim 1, wherein the catalyst system (6) is a catalyst system comprising both of a molding containing the component (A) with the catalyst carrier component obtained by integrally molding and a molding containing a component (B) obtained by integrally molding.

42. The process according to ~~any one of~~ claim 1 (6) and claims 34 to 41, wherein the component (B) is  $\alpha$ -alumina.

43. The process according to ~~any one of~~ claim 1 (6) and claims 34 to 42, wherein the component (A) is a component containing ruthenium.

44. The process according to claim 43, wherein the component (A) is a component containing ruthenium oxide.

45. The process according to ~~any one of~~ claims 43 to 44, wherein the component (B) and/or the catalyst carrier

component is a component containing titanium oxide.

46. The process according to claim 1, wherein the catalyst (7) is an outer surface-supported catalyst obtained by supporting ruthenium oxide on a carrier at the outer surface.

47. The process according to claim 1, wherein the catalyst (8) is an outer surface-supported catalyst prepared by an alkali preliminary impregnation process.

48. The process according to claim 1, wherein the catalyst (9) is a ruthenium oxide catalyst supported on chromium oxide.

49. The process according to claim 1, wherein the catalyst (9) is a catalyst obtained by calcining a ruthenium chloride catalyst supported on chromium oxide.

50. A process for producing a supported ruthenium oxide catalyst selected from the following processes (1) to (5):

(1) a process for producing a supported ruthenium oxide catalyst, which comprises the steps of supporting a ruthenium compound on a carrier, treating the supported one by using a basic compound, treating by using a reducing compound, and oxidizing;

(2) a process for producing a supported ruthenium oxide catalyst, which comprises the steps of supporting a ruthenium compound on a carrier, treating the supported one

by using a reducing compound to form ruthenium having an oxidation number of 1 to less than 4 valence, and oxidizing;

(3) a process for producing a supported ruthenium oxide catalyst, which comprises the steps of supporting a ruthenium compound on a titanium oxide carrier containing rutile titanium oxide, treating the supported one by using a reducing agent, and oxidizing;

(4) a process for producing a supported ruthenium oxide catalyst, which comprises the steps of supporting a ruthenium compound on a titanium oxide carrier containing an OH group in an amount of  $0.1 \times 10^{-4}$  to  $30 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier, treating the supported one by using a reducing agent, and oxidizing; and

(5) a process for producing a supported ruthenium oxide catalyst containing ruthenium oxide only at an outer surface layer, not less than 80% of the outer surface of said catalyst satisfying the following expression (1):

$$S/L < 0.35 \quad (1)$$

wherein L is a distance between a point (A) and a point (B), said point (B) being a point formed on the surface of a catalyst when a perpendicular line dropped from any point (A) on the surface of the catalyst to the inside of the catalyst goes out from the catalyst at the opposite side of the point (A), and S is a distance between the point (A) and a point (C), said point (C) being a point on the

perpendicular line where ruthenium oxide does not exist, wherein said process comprises supporting an alkali on a carrier, supporting at least one ruthenium compound selected from the group consisting of ruthenium halide, rutheniumoxy chloride, ruthenium-acetylacetonato complex, ruthenium organic acid salt and ruthenium-nitrosyl complex on the carrier, treating by using a reducing agent, and oxidizing.

51. The process according to claim 50 (2), wherein said process comprises the steps of supporting at least one ruthenium compound selected from the group consisting of ruthenium halide, chlororuthenate salt, oxyruthenate salt, rutheniumoxy chloride, ruthenium-ammine complex, chloride of ruthenium-ammine complex, ruthenium-acetylacetonato complex, ruthenium organic acid salt and ruthenium-nitrosyl complex on a carrier, treating the supported one by using a reducing agent to form ruthenium having an oxidation number of 1 to less than 4 valence, and oxidizing.

52. The process according to claim 50 (2), wherein said process comprises the steps of supporting at least one ruthenium compound selected from the group consisting of ruthenium halide, chlororuthenate salt, oxyruthenate salt, rutheniumoxy chloride, ruthenium-ammine complex, chloride of ruthenium-ammine complex, ruthenium-acetylacetonato complex, ruthenium organic acid salt and ruthenium-

nitrosyl complex on a carrier, treating the supported one by using a basic compound, treating by using a reducing agent, and oxidizing.

53. The process according to claim 50 (2), wherein the reducing agent is a reducing compound.

54. The process according to claim 50 (1) or (2), wherein said process comprises supporting ruthenium halide on a carrier, adding an alkali to the supported one, treating by using a reducing compound, and oxidizing.

55. The process according to claim 50 (1) or (2), wherein said process comprises supporting ruthenium halide on a carrier, treating the supported one by using an alkali solution of a reducing compound, and oxidizing.

56. The process according to claim 50 (1) or (2), wherein said process comprises supporting ruthenium halide on a carrier, adding an alkali to the supported one, treating by using a reducing compound, adding an alkali metal chloride, and oxidizing.

57. The process according to claim 50 (1) or (2), wherein said process comprises supporting ruthenium halide on a carrier, treating the supported one by using an alkali solution of a reducing compound, adding an alkali metal chloride, and oxidizing.

58. The process according to claim 50 (1) or (2), wherein said process comprises supporting ruthenium halide

on a carrier, adding an alkali to the supported one, treating by using hydrazine, and oxidizing.

59. The process according to claim 50 (1) or (2), wherein said process comprises supporting ruthenium halide on a carrier, treating the supported one by using an alkali solution of hydrazine, and oxidizing .

60. The process according to claim 50 (1) or (2), wherein said process comprises supporting ruthenium halide on a carrier, adding an alkali to the supported one, treating by using hydrazine, adding an alkali metal chloride, and oxidizing.

61. The process according to claim 50 (1) or (2), wherein said process comprises supporting ruthenium halide on a carrier, treating the supported one by using an alkali solution of hydrazine, adding an alkali metal chloride, and oxidizing.

62. The process according to claim 50, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by using titanium oxide containing not less than 10% by weight of rutile titanium oxide as a carrier.

63. The process according to claim 50, wherein the catalyst (1) or (2) is a supported ruthenium oxide catalyst obtained by using titanium oxide containing not less than 30% by weight of rutile titanium oxide as a carrier.

64. The process according to claim 50 (3) or (4),



wherein the titanium oxide is titanium oxide containing not less than 10% of rutile titanium oxide.

65. The process according to claim 50 (3) or (4), wherein the titanium oxide is titanium oxide containing not less than 30% of rutile titanium oxide.

66. The process according to claim 50 (3) or (4), wherein said process comprises supporting a ruthenium compound on a carrier, reducing the supported one by using a reducing hydrogenated compound, and oxidizing.

67. The process according to claim 50 (3) or (4), wherein said process comprises supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound, and oxidizing.

68. The process according to claim 50 (3) or (4), wherein said process comprises supporting a ruthenium compound on a carrier, treating the supported one by using an alkali solution of a reducing compound, and oxidizing.

69. The process according to claim 50 (3), wherein the catalyst is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $0.1 \times 10^{-4}$  to  $30 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

70. The process according to claim 50 (3), wherein the catalyst is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $0.2 \times 10^{-4}$  to  $20 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

71. The process according to claim 50 (3), wherein the catalyst is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $3 \times 10^{-4}$  to  $15 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

72. The process according to claim 50 (3) or (4), wherein the catalyst is obtained by supporting a ruthenium halide on carrier, treating the supported one by using a reducing compound, and oxidizing.

73. The process according to claim 50 (3) or (4), wherein the catalyst is obtained by supporting a ruthenium halide on carrier, treating the supported one by using an alkali solution of a reducing compound, and oxidizing.

74. The process according to claim 50 (4), wherein the

catalyst is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $0.2 \times 10^{-4}$  to  $20 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

75. The process according to claim 50 (4), wherein the catalyst is a supported ruthenium oxide catalyst obtained by the steps which comprise supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound or a reducing agent in a liquid phase, and oxidizing, wherein titanium oxide containing an OH group in an amount of  $3 \times 10^{-4}$  to  $15 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

76. A supported ruthenium oxide catalyst obtained by supporting on a titanium oxide carrier containing not less than 20% by weight of rutile titanium oxide.

77. The catalyst according to claim 76, wherein the content of rutile titanium oxide is not less than 30% by weight.

78. The catalyst according to claim 76, wherein the content of rutile titanium oxide is not less than 80% by weight.

79. The catalyst according to claim 76, wherein the

content of rutile titanium oxide is not less than 90% by weight.

*Sub B2*  
80. The catalyst according to claim 76, wherein titanium oxide containing an OH group in an amount of  $0.1 \times 10^{-4}$  to  $30 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

81. The catalyst according to claim 76, wherein titanium oxide containing an OH group in an amount of  $0.2 \times 10^{-4}$  to  $20 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

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82. The catalyst according to claim 76, wherein titanium oxide containing an OH group in an amount of  $3 \times 10^{-4}$  to  $10 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.

83. The catalyst according to claim 76, which is a supported ruthenium oxide catalyst obtained by supporting a ruthenium compound on a carrier, reducing the supported one by using a reducing hydrogenated compound, and oxidizing.

84. The catalyst according to claim 76, which is a supported ruthenium oxide catalyst obtained by supporting a ruthenium compound on a carrier, treating the supported one by using a reducing compound, and oxidizing.

85. The catalyst according to claim 76, which is a supported ruthenium oxide catalyst obtained by supporting

a ruthenium compound on a carrier, treating the supported one by using an alkali solution of a reducing compound, and oxidizing.

~~86. The catalyst according to claim 78, wherein titanium oxide containing an OH group in an amount of  $3 \times 10^{-4}$  to  $10 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.~~

~~87. The catalyst according to claim 79, wherein titanium oxide containing an OH group in an amount of  $3 \times 10^{-4}$  to  $10 \times 10^{-4}$  (mol/g-carrier) per unit weight of a carrier is used as the carrier.~~